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PHASE CHANGES IN THE NIOBIUM-HYDROGEN SYSTEM. I. ACCOMMODATION --ETC(U)
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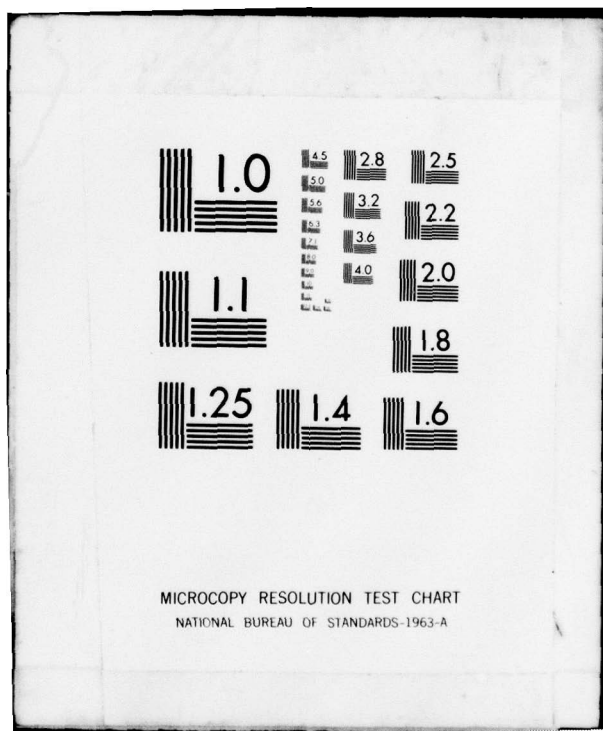
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ACCOMMODATION EFFECTS DURING HYDRIDE PRECIPITATION.

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10 B. J. Makenas H. K. Birnbaum

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University of Illinois at Urbana-Champaign
Department of Metallurgy and Mining Engineering
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PHASE CHANGES IN THE NIOBIUM-HYDROGEN SYSTEM I:
ACCOMMODATION EFFECTS DURING HYDRIDE PRECIPITATION

B. J. Makenas⁺ and H. K. Birnbaum

University of Illinois at Urbana-Champaign
Department of Metallurgy and Mining Engineering
Urbana, Illinois 61801

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⁺Present Address: Hanford Engineering and Development Laboratory,
Westinghouse-Hanford, Box 1970, Bldg. 3190, Richland, WA 99352.

ABSTRACT

The accommodation effects which accompany hydride precipitation were studied in the Nb-H system using T.E.M. Elastic accommodation and punching of prismatic dislocation loops in the solid solution matrix were observed on precipitation. The reversibility of the plastic accommodation processes was studied. Dislocation generation and motion in the hydride was observed during reversion. These observations were related to the volume changes due to hydride formation and to the thermodynamics of the phase change.

Direct evidence for the inhibition of hydride precipitation due to trapping at O and N interstitials is presented.

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I. INTRODUCTION

Precipitation of hydrides has been shown to play an important role in the hydrogen embrittlement of a number of alloys. In systems such as Nb-H fracture occurs by a stress-induced hydride cleavage mechanism (1-5) and the thermodynamics of hydride precipitation in an external stress field (6-9) plays an important role in this embrittlement process. As a result of the sensitivity of hydride precipitation to stress, embrittlement can occur at temperatures well in excess of the solvus temperatures observed at zero stress (2-4). Elastic stresses applied during cooling can induce hydride precipitation above the stress-free solvus (7-9) and can cause hydride re-resolution and precipitation in a more favorable orientation relative to the external stress. In most systems the volume change on hydride formation is accommodated by elastic deformation of the matrix and the precipitate as well as by plastic deformation of the solid solution matrix around the hydride (7,10). It has been shown that hydride precipitation occurs preferentially along slip bands (2,11); an effect which is particularly marked if the slip bands form during the cooling process.

In order to calculate the effects of stress on the thermodynamics of hydride forming systems, it is necessary to more fully understand the accommodation processes. As previously discussed (7), the elastic accommodation is reversible while the plastic accommodation processes are irreversible and must occur on both hydride

precipitation and on reversion. It is the purpose of the present paper to examine the nature of these plastic accommodation processes and to relate them to the thermodynamics of the hydride systems. We will use the Nb-H system as a model system but the results are expected to be more generally applicable.

In the Nb-H system (12) the solid solubility is about 4 at.% at room temperature and decreases markedly as the temperature is decreased. On cooling, the β hydride precipitates as plates whose habit is the {100} of the parent α b.c.c. solid solution (7,13). A variety of other morphologies are observed on nonequilibrium cooling (7). In all cases plastic deformation of the α solid solution accompanies the hydride formation and this plastic accommodation results in a very large thermal hysteresis on reversion. The β hydride has a f.c. orthorhombic structure (14) for which there are six variants relative to the parent α . Each β precipitate generally contains several of these variants which are twin related across {110} domain boundaries (15). The presence of multiple domains in each hydride plate reflects the minimization of the elastic strain at the interface in a manner similar to that discussed for the b.c.c. \rightarrow f.c. orthorhombic martensitic transformation (16).

II. EXPERIMENTAL PROCEDURE

IIA. Specimen Preparation

Westlake demonstrated that electropolishing of hydrogen-charged refractory metals can significantly increase or decrease

the hydrogen concentration depending on the detailed thinning procedure (17) and therefore, controlled compositions of hydrogen cannot be maintained on thinning precharged specimens. In addition, acid electropolishing techniques are known to preferentially attack second phases such as hydride precipitates. For these reasons, hydrogen was introduced into niobium samples only after all thinning procedures had been completed. Niobium strips were UHV outgassed at 2400 K and 7.5×10^{-7} Pa (10^{-10} torr) to remove oxygen and nitrogen impurities. A typical analysis for impurities is given in Table 1. Discs, 3 mm in diameter, were cut from the outgassed sheet, jet thinned from both sides using H_2SO_4 :HF:methanol, 2:1:7, at 100-125 volts and electropolished to perforation in a solution of H_2SO_4 :HF:lactic acid, 1:1:2 at 3 volts using an aluminum cathode. Hydrogen charging to controlled concentrations was accomplished using a palladium coating technique (18) to remove the oxide permeation barrier and gas phase or electrolytic charging techniques. The Pd layer was removed immediately after charging by immersion in mercury. This palladium coating technique was necessary because of oxygen pickup during gas-phase charging (19) and the lack of reproducibility of the usual cathodic charging methods. Hydrogen analysis was carried out using vacuum extraction methods after examination in the T.E.M.

IIB. Beam Heating Effects

During in situ cooling of low H concentration samples, precipitation of β hydride always occurred first in thin areas not

illuminated by the electron beam. As a consequence, an area several microns in diameter could be kept free of hydride until the electron beam was removed. At normal 200 kV operation and low beam currents, the electron beam had no effect on already existing hydrides, except very near the solvus temperature. A lower accelerating voltage of 100 kV or operation without a condenser aperture caused rapid movement of domain boundaries within hydrides.

These effects are attributable to electron beam heating of a small area of the sample. Thermal gradients are created within the specimen and mobile solutes having a positive heat of transport, such as hydrogen (20), will tend to migrate toward the cooler areas of the specimen establishing concentration gradients which make precipitation unlikely in the area under observation. The magnitude of this effect can be estimated using

$$\text{grad } C = - \frac{CQ^*}{kT^2} \text{ grad } T \quad (1)$$

to describe the thermal transport of hydrogen, and

$$\Delta T = \left(\frac{\Delta E}{t} \right) \frac{I}{4\pi K} \left[0.577 + 2 \ln \frac{R}{a} \right] \quad (2)$$

to describe (21) the thermal gradient in the specimen. In the above relations C is the hydrogen concentration, T is the temperature, Q^* is the heat of transport, R is the radial distance between the electron beam and the thermal sink provided by the stage, I is the total electron beam current, t is the specimen thickness,

K is the specimen thermal conductivity and k is Boltzmann's constant. The parameter β is equal to $(H \ln \sqrt{2})/2$ where H is the diameter at half maximum of the Gaussian beam profile. The energy loss per electron, ΔE , can be calculated (22). Using the parameters suitable for the present experiments at 200 kV, $\Delta E/t \approx 0.75 \times 10^{16}$ eV/cm, $I \approx 2.3 \times 10^{12}$ electrons/second, and $H \approx 2 \mu\text{m}$, the beam heating is estimated to be about 7 K. For a hydrogen concentration of 10^{-3} this results in a decrease of hydrogen concentration under the beam of $\Delta C/C \approx -0.4$ which is large enough to account for the lack of precipitation observed.

III. RESULTS AND DISCUSSION

IIIA. Accommodation Effects

Plastic accommodation of the molal volume change, $\Delta V_{\alpha\beta}$, which accompanies β hydride precipitation was observed on rapidly cooling thinned specimens with H/Nb in the range of 0.001 to 0.02 to 77 K and then warming to 300 K. The structures (Figs. 1-3) consisted of approximately spherical volumes of high density dislocation tangles, 1 to 2 μm in diameter, surrounded by dislocation loops emitted in $\langle 111 \rangle$ directions. These were shown to be prismatic loops having $\langle 111 \rangle$ Burgers vectors in agreement with Schober (10). Analysis using "inside-outside" contrast techniques showed these to be interstitial in nature. Since $\Delta V_{\alpha\beta} > 0$ these interstitial loops formed during cooling. No prismatic vacancy loops, which might form during hydride reversion

when $\Delta V_{\alpha\beta} < 0$, were observed, suggesting that the plastic accommodation during reversion did not occur by prismatic loop punching.

In order to study the actual hydride precipitation and to observe any differences between precipitation in thin and thick foil areas, hydrogen-charged samples were cooled in the T.E.M. at rates of 3 to 20 degrees K/minute. At these cooling rates, hydride precipitation did not occur as discrete β particles. Instead, all of the hydride formed as a highly deformed ring around the central perforation in the thinnest portion of the foil (Fig. 4). This region was identified as the β hydride from the electron diffraction pattern and from the presence of domain boundaries. Attempts were made to "innoculate" the specimen with a distribution of nucleation sites produced by rapidly quenching the specimen to form small hydrides followed by dissolution on warming. On slow cooling, following this inoculation treatment, the hydride still formed only in the thinnest sections, and at nucleation sites nearest the central perforation. This inability to form the hydride throughout the specimen volume on slow cooling reflects the high hydrogen diffusivity and the tendency of the hydride to form in the thinnest part of the foil in order to minimize its accommodation free energy. In effect the α - β solvus temperature is highest in the thinnest regions of the sample. Effects of volume constraints on the hydride formation were also seen in the distribution of hydride precipitation sizes in a H/Nb = 0.10 foil quenched to 77 K. In the thinnest foil sections

the hydride precipitate diameters were 4-5 μm while in foil regions of about 1000-2000 \AA thickness the sizes were 1-2 μm .

Precipitation of β hydride from solid solution is accompanied by a molal volume expansion, $\Delta V_{\alpha\beta}$, of approximately 12 percent. As previously discussed (7-9), this expansion is accommodated by elastic and plastic work done in the matrix and in the hydride. The free energy for precipitation $\Delta G_{\alpha\beta}$ is then

$$\begin{aligned} \Delta G_{\alpha\beta} = & \Delta G_{\alpha\beta}(\text{chemical}) + \Delta G(\text{plastic}) \\ & + \Delta G(\text{elastic}) + \Delta G(\text{surface}) \end{aligned} \quad (3)$$

where $\Delta G_{\alpha\beta}(\text{chemical})$ is the molal free energy for the unconstrained α - β transition, $\Delta G(\text{elastic})$ is the elastic work done in the matrix and in the precipitate due to $\Delta V_{\alpha\beta}$, $\Delta G(\text{surface})$ is the energy to create the interface between precipitate and matrix, and $\Delta G(\text{plastic})$ is the plastic work done in the matrix due to $\Delta V_{\alpha\beta}$. In the α - β transition the observations indicate that all of the plastic work is done in the α phase.

For precipitation of the hydride, the plastic work term, $\Delta G(\text{plastic})$, is the energy required to create prismatic interstitial dislocation loops at the α - β interface and to move these loops into the matrix thus transporting Nb atoms away from the growing precipitate. As noted by Brown et al. (23), dislocation loops will not be observed unless the stress at the α - β interface is sufficiently large to nucleate dislocation loops. The maximum shear stress at the interface of an ellipsoidal particle, σ_s , is

$$\sigma_s = 2\mu e^T/3 \quad (4)$$

where μ is the matrix shear modulus and e^T is the magnitude of the dilatational strain associated with the transformation. In the case of the α - β transition $\sigma_s \approx \mu/40$ and is therefore large enough to nucleate dislocation loops and to cause the hydride to become incoherent at the earliest stages of precipitation.

A molal volume decrease $\Delta V_{\beta\alpha}$ of about 12 percent occurs on reversion of the hydride and an equation equivalent to Eqn. (3) may be written to describe the reversion. In this case however, $\Delta G_{\text{elastic}} < 0$ and $\Delta G_{\text{surface}} < 0$ as these energy terms are reversible on hydride dissolution and aid the reversion. As pointed out by Birnbaum et al. (7), the large thermal hysteresis on precipitation and reversion of the hydride in the Nb-H system reflects the large positive $\Delta G(\text{plastic})$ free energy terms for both precipitation and reversion of the hydrides.

Accommodation processes during hydride reversion were studied on slowly heating from 77 K after forming the hydrides by rapid cooling. As shown in Fig. 5 the hydride initially had a very low dislocation density and was surrounded by a dense dislocation array and prismatic interstitial loops in the adjacent α solid solution. As the hydrides decreased in size during heating, the $\Delta V_{\beta\alpha}$ caused dislocations having $\langle 111 \rangle$ Burgers vectors to precede the α - β interface into the interior of the β precipitate. The process continued until the entire precipitate filled with dislocation tangles (Figures 6 and 7). While the actual α - β interface could not usually be observed due to the high dislocation densities, selected area diffraction confirmed that

dislocation motion occurred quite readily within existing hydrides. The β domain boundaries did not appear to hinder this motion. The accommodation dislocations did not appear as prismatic loops but may have been loops which intersected the foil surfaces. Since the dislocation motion was from the α - β interface towards the hydride center, such prismatic loops would have been interstitial in nature. Alternatively, if they are shear dislocation their correlated motion could have the effect of moving material towards the center of the β hydride as reversion occurs.

While it is theoretically possible for the volume accommodation of $\Delta V_{\beta\alpha}$ which accompanies hydride dissolution to be accomplished by the punching of vacancy prismatic dislocation loops in the α matrix or by the absorption of existing prismatic interstitial loops at the α - β interface, neither of these two mechanisms was observed. Presumably interactions between the existing prismatic dislocations inhibit the absorption of the interstitial loops during reversion. The lack of plastic accommodation by means of prismatic vacancy loop punching in the α matrix may also be caused by the presence of dislocation tangles at the α - β interface formed during precipitation. In a few cases the dislocation density was low enough to permit direct observation of the α - β interface during reversion. Some additional dislocation density was observed to remain in the volume traversed by the α - β interface.

The magnitude of the plastic work term during precipitation, $\Delta G(\text{plastic})$, was estimated from the number and position of prismatic interstitial loops. $\Delta G(\text{plastic})$ consists primarily of loop formation energy, the work of loop motion away from the

precipitate and the loop interaction energies. These terms can be written (24):

$$\begin{aligned} \Delta G(\text{plastic}) = & \sum_i \frac{R_i \mu b^2}{2(1-\nu)} \left(\ln \frac{4R_i}{\rho} - 1 \right) + \sum_i 2\pi R_i \sigma b d_i \\ & + \sum_i \sum_j \frac{\mu b^2}{(1-\nu)} \left(\frac{R_i + R_j}{2} \right) k_{ij} (K_{ij} - E_{ij}) \end{aligned} \quad (5)$$

where μ is the shear modulus, b is the Burgers' vector, R_i is the radius of the i^{th} dislocation, d_i is the distance the i^{th} dislocation has moved from the precipitate, ν is Poisson's ratio, ρ is about $b/8$, σ is the flow stress of the solid solution, and the summations are carried out over all of the dislocation loops. In the loop interaction energy term the parameter

$$k_{ij}^2 = \frac{4 \left(\frac{R_i + R_j}{2} \right)^2}{z_{ij}^2 + 4 \left(\frac{R_i + R_j}{2} \right)^2} \quad (6)$$

where z_{ij} is the separation of the i^{th} and j^{th} loops. The elliptic integrals are

$$\begin{aligned} E_{ij} &= \int_0^{\pi/2} (1 - k_{ij}^2 \sin^2 \eta)^{1/2} d\eta \\ K_{ij} &= \int_0^{\pi/2} (1 - k_{ij}^2 \sin^2 \eta)^{-1/2} d\eta \end{aligned} \quad (7)$$

The summations are carried out over all of the dislocation loops. Using Eq. (5) and the information obtained from micrographs, a

plastic work term of 210 J/mole is estimated for the hydrides formed in the thin films. This value is of the same magnitude but less than the value of approximately 1260 J/mole estimated by Birnbaum et al. (7) for precipitation in massive specimens. The calculated value is a lower bound for $\Delta G(\text{plastic})$ since:

- (a) the calculation does not account for the generation of loops on slip systems which allow loss of loops through the surface. In the thin foils, loops were usually observed in only two of the six $\langle 111 \rangle$. Correction for the dislocation loss would increase the plastic work term to about 630 J/mole.
- (b) The energy of the tangle of interfacial dislocations at the precipitate interface has not been included in the calculation; and
- (c) the adjacent free surfaces reduce the elastic energy and therefore the need for some of the plastic accommodation which is driven by the elastic energy.

The behavior described above for the Nb-H system can be compared with that observed for a variety of other hydride forming systems as shown in Table II. Since a large volume change on precipitation of the hydride requires both elastic and plastic accommodation, this precipitation occurs at temperatures below the true thermodynamic equilibrium temperature, i.e., the equilibrium temperature for unconstrained hydrides (7). Reversion of the hydride on heating is aided by the recovery of the elastic accommodation energy. Plastic accommodation energy, which is stored

in the form of dislocation configurations can aid the reversion only if the plastic processes are reversible. If this occurs, reversion may also take place below T_e and the hysteresis loop is expected to be quite small. This appears to be the case for the V-H system for which the thermal hysteresis $(T_r - T_s)/T_s \approx 0.009$ (T_r = temperature at which hydride reversion is complete on heating and T_s = solvus temperature at which hydride precipitation begins on cooling). In the V-H system (35) the hydride forms in thin plates and only a low density of interfacial dislocations and shear dislocations ($\vec{b} \parallel \langle 111 \rangle$) form. The $\Delta V/V_0$ is relatively small and appears to be accommodated primarily by elastic processes. In contrast to this behavior both elastic and plastic accommodation processes are observed (9,27,28,39) in the Zr-H and Ti-H systems. The dislocations generated are predominantly shear loops with $\vec{b} \parallel \langle 11\bar{2}0 \rangle$ and on reversion of the hydride, a partial recovery of the plastic accommodation dislocations occurs. As a result of the increased plastic work, the thermal hysteresis is larger, $\Delta T/T_s \approx 0.08$. The partial dislocation recovery on reversion does reduce the value of $\Delta T/T_s$ from that which would be observed in the absence of recovery. Strengthening of the Ti matrix by alloying (9) has the effect of increasing the thermal hysteresis to $\Delta T/T_s \approx 0.26$. In the Nb-H system the large thermal hysteresis, $\Delta T/T_s \approx 0.11$ (41) is a consequence of the large amount of plastic work which occurs both on precipitation and reversion. Little recovery of the prismatic dislocation loops was observed, in contrast to the behavior of shear loops in the Zr-H and Ti-H systems, presumably due to a

higher lattice friction stress for the prismatic loops.

IIIB. Trapping Effects

Several investigators, using internal friction and resistivity measurements, have found evidence for trapping of hydrogen by oxygen and nitrogen interstitials in niobium with binding enthalpies of 0.08 (44) and 0.12 eV/atom (45), respectively. While it is expected that this trapping interaction should affect the hydride solvus, this has been a matter of some controversy. Chang and Wert (46) and Westlake and Ockers (47) both found shifts in the solvus to lower temperatures for oxygen additions in the vanadium-hydrogen system, but they differ on the magnitude of the effect. Lecocq (48) however found no effect of oxygen on the tantalum hydride solvus while Pfeiffer and Wipf (45) found solvus shifts and decreasing amount of niobium hydride precipitation with N additions to niobium.

To demonstrate the effect of O and N interstitials upon hydride precipitation, T.E.M. samples were made from niobium which had been doped with 0.27 atomic percent oxygen and 0.47 atomic percent nitrogen. These samples were then electrolytically charged to 0.1 and 0.7 atomic percent hydrogen, respectively. During subsequent in situ cooling to 77°K, no hydride precipitation was observed in either foil. The hydrogen trapped at O or N is evidently not available for the hydride precipitation process in agreement with the measurements of Pfeiffer and Wipf (45). These observations support their conclusions that the amount of hydride precipitation decreases with increasing solute trap concentrations.

IV. SUMMARY AND CONCLUSIONS

The accommodation processes which play such an important role in determining the thermodynamics of precipitation in metal-hydrogen systems were shown to be markedly different during precipitation and during reversion. During precipitation of the β hydride from the α solid solution the volume increase was accommodated elastically and by punching of prismatic interstitial loops in the α phase. The energy of plastic accommodation calculated from this loop punching is in reasonable agreement with that estimated from thermodynamic arguments. During hydride reversion the volume decrease was accommodated primarily by recovery of the elastic strain and by dislocation processes in the β hydride. The necessity for plastic work in the hydride is consistent with the large thermal hysteresis observed on reversion.

Direct confirmation of hydrogen trapping at O and N interstitials with a trapping energy large enough to prevent precipitation of the hydride was obtained.

TABLE 1

IMPURITY ANALYSIS OF NIOBIUM SPECIMENS

| Spark Source Mass Spectrometer Analysis | |
|---|----------------------------|
| <u>Solute Element</u> | <u>Concentration (ppm)</u> |
| Si | 4.0 |
| Ti | 0.1 |
| V | 0.2 |
| Cr | 0.04 |
| Mn | 0.03 |
| Fe | 0.03 |
| Cu | 0.1 |
| Zn | 0.06 |
| Mo | 0.4 |
| Ta | 10.0 |
| W | 5.0 |

| Vacuum Fusion Analysis | |
| Solute Element | Concentration (at.%) |
| O | 0.03 |
| N | 0.02 |
| C | undetectable |

TABLE II

ACCOMMODATION EFFECTS IN HYDRIDE PRECIPITATION

| | Nb-H | V-H | Zr-H | Ti-H | Ti 10%Al-H |
|--|--|--|---|--------------------------------|---|
| Hydride Structure | β (14) f.c.c. orthorhombic | β (25,26) monoclinic | γ (27) f.c.c. tetragonal | γ f.c.c. flourite | γ f.c.c. flourite |
| Volume Change on Precipitation $\Delta V/V_0$ | 0.12 (29) | 0.062 (30) | 0.12 (31) | 0.18 (32) | 0.18 (32) |
| Hydride Morphology | plates // (001) (13) | plates // γ (227) (32-35) | needles // $\langle 11\bar{2}0 \rangle$ (36,38) | -- | plates // $\{10\bar{1}0\}$ (37) |
| Plastic Accommodation | prismatic loops $\vec{b} = a/2 \langle 111 \rangle$ tangled interface dislocations (present work) | interface disl. $\vec{b} // \langle 111 \rangle$ low density of shear disl. $\vec{b} // \langle 111 \rangle$ (35) | shear disl. (27,36,38) $\vec{b} // \langle 11\bar{2}0 \rangle$ prismatic loops $\vec{b} // \langle 11\bar{2}0 \rangle$ | -- | shear disl. $\vec{b} // \langle 11\bar{2}0 \rangle$ (9,39) |
| Dislocation Behavior on Reversion | disl. motion in β hydride (present work) | -- | partial recovery in α solid solution (40) | -- | partial recovery in α solid solution (9) |
| Thermal Hysteresis $\Delta T/T_s$ | 0.11 (41) | 0.009 (42) | 0.081 (43) | 0.041 (9) | 0.26 (9) |

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FIGURE CAPTIONS

- Figure 1a and 1b The prismatic loops and dislocation tangles formed during the precipitation and dissolution of fast cooled hydrides.
- Figure 2 High magnification micrograph of interstitial prismatic loops associated with the precipitation of β hydride.
- Figure 3 The dislocation remnants of a large hydride which had nucleated on a low angle grain boundary.
- Figure 4 The preferential precipitation of hydride in the thinnest areas of the foil after slow cooling to 147 K for an $\text{NbH}_{0.01}$ alloy. The hydride is in the lower half of the micrograph.
- Figure 5 A portion of a large hydride precipitate formed on quenching to 77 K from a charging temperature of 383 K. The foil composition is $\text{NbH}_{0.1}$. The hydride contains little deformation and domain boundaries are visible. The interface is highly deformed and plastic deformation extends into the matrix.

Figure 6a

A hydride precipitate formed in a thick foil area by quenching to 77 K from a charging temperature of 383 K. Foil composition $H/Nb = 0.10$.

Figure 6b

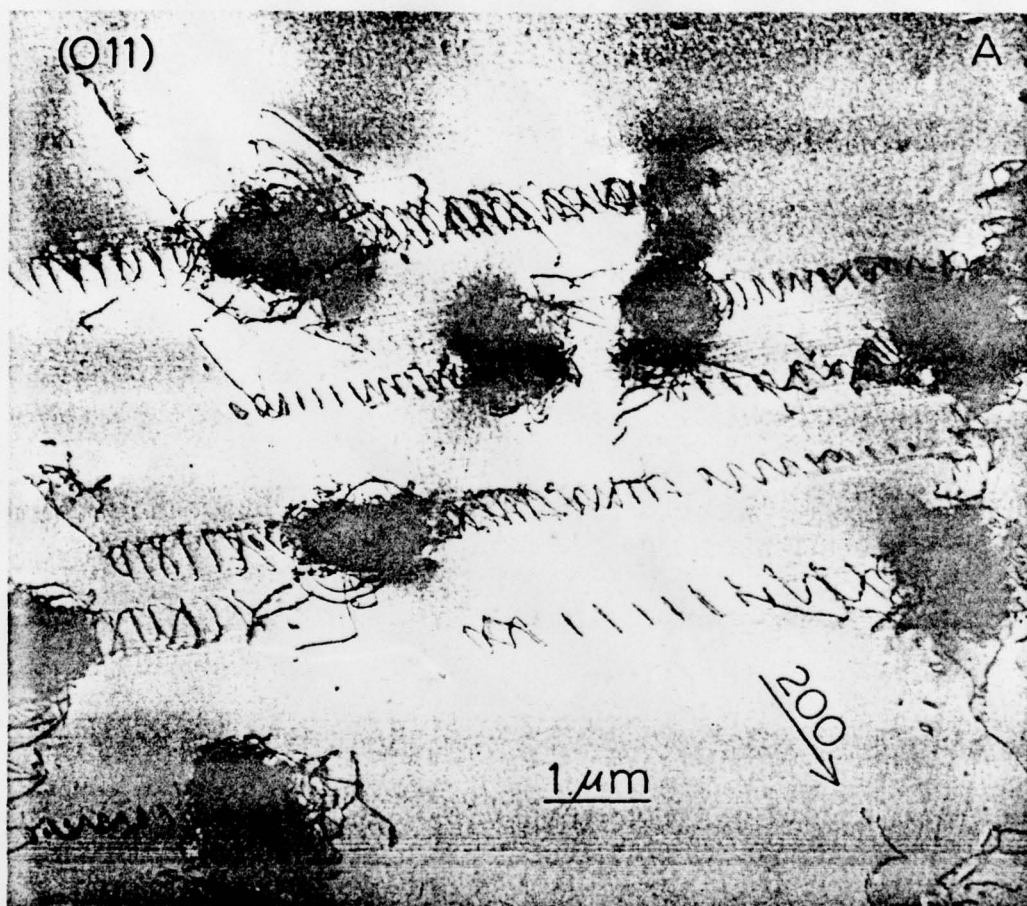
Same area as above after heating to 333 K to dissolve the hydride precipitate.

Figure 7a

A large hydride precipitate undergoing dissolution at 333 K.

Figure 7b

Same as Figure 7a above at higher magnification. Dislocations are in motion towards the center of the precipitate. $H/Nb = 0.10$.



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Fig. 1a



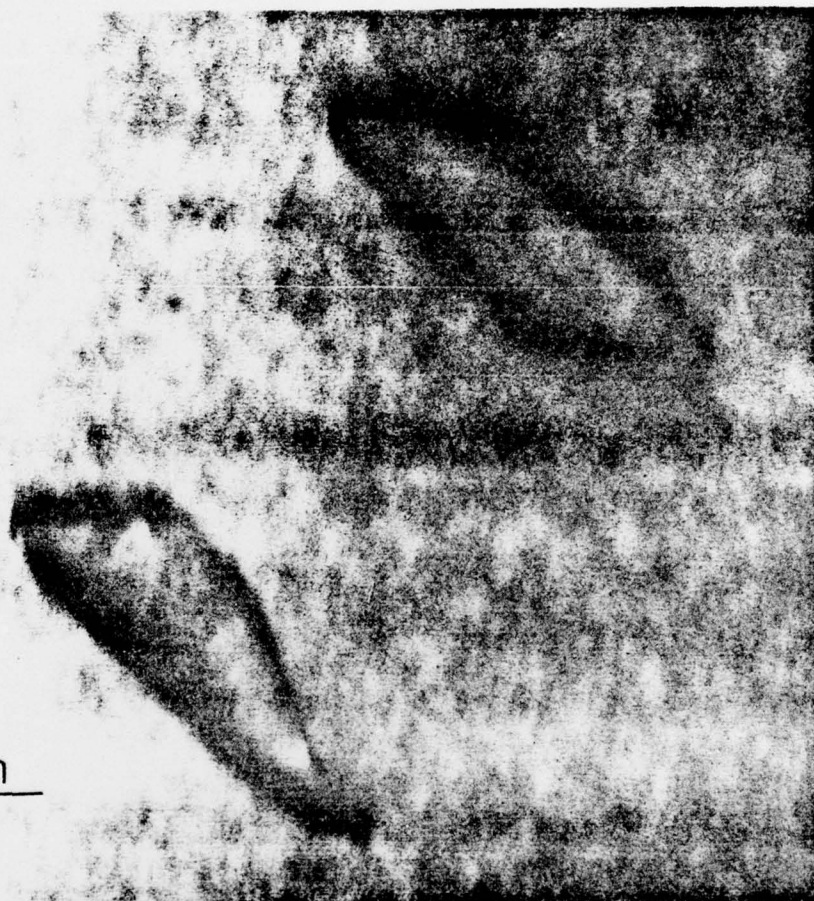
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Fig. 1b

(011)

\nearrow
200

0.1 μ m



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Fig. 2



Fig. 3

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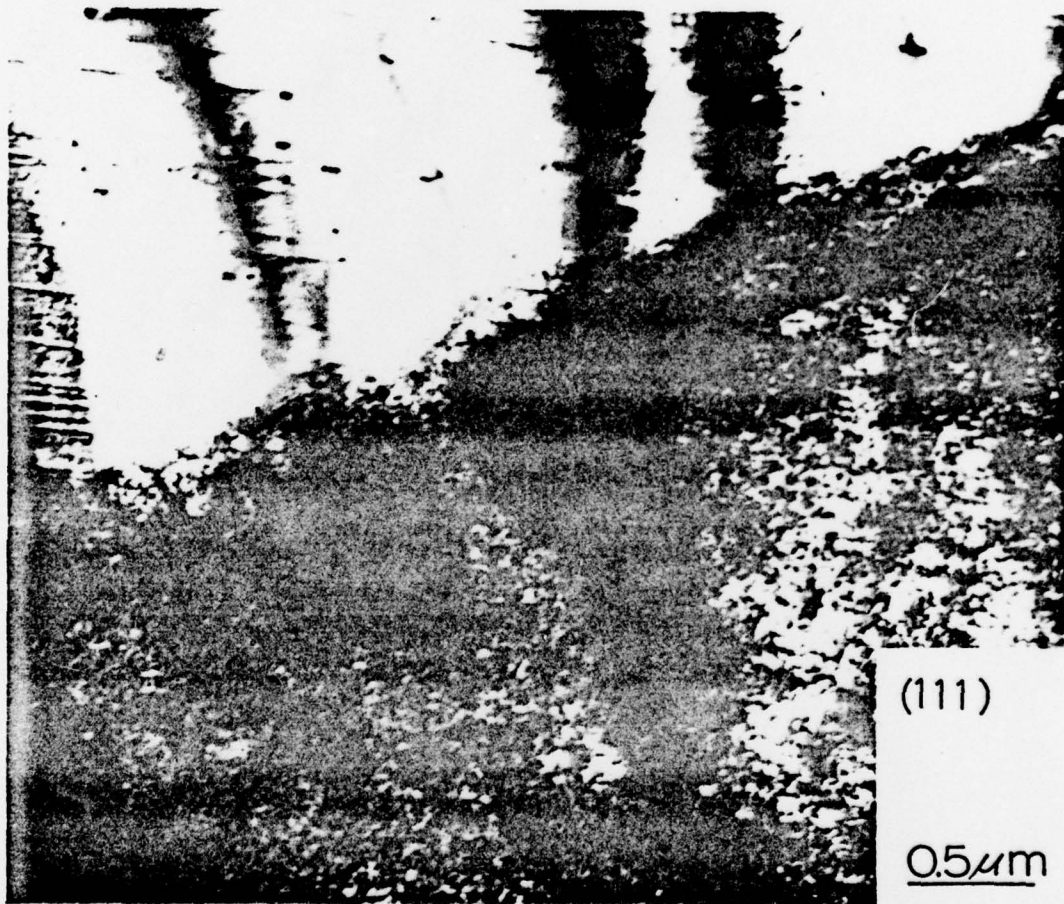
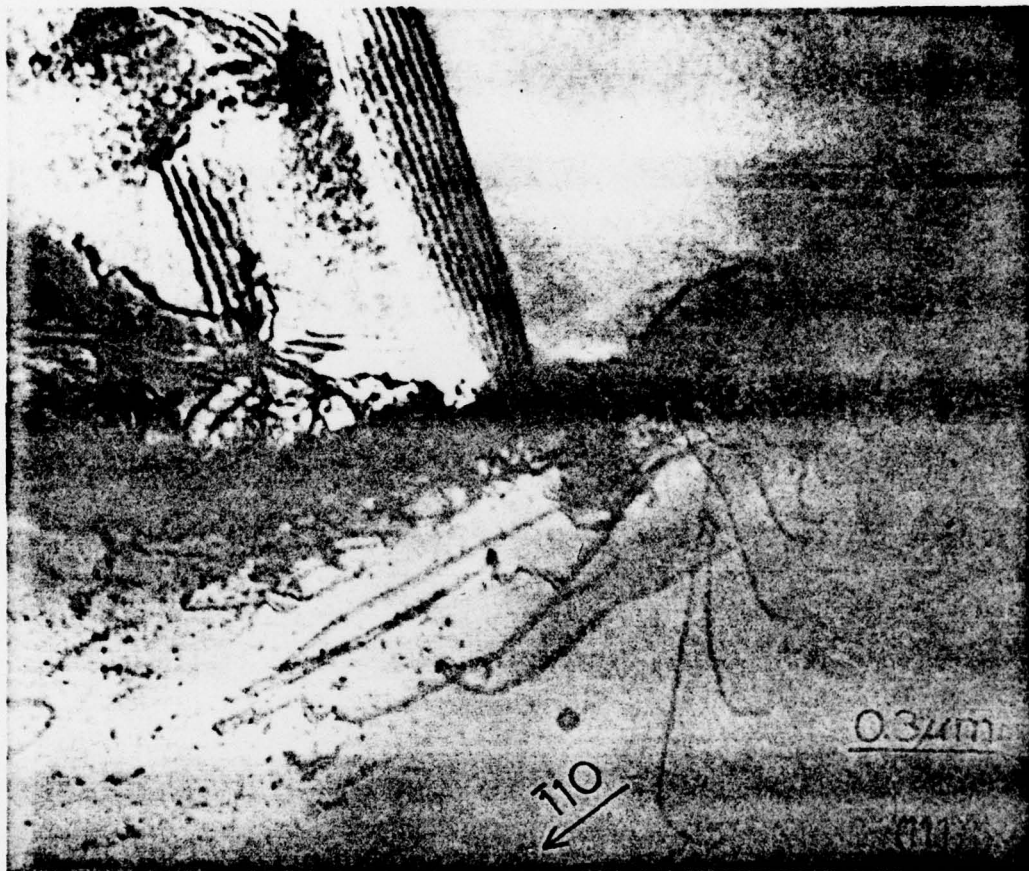


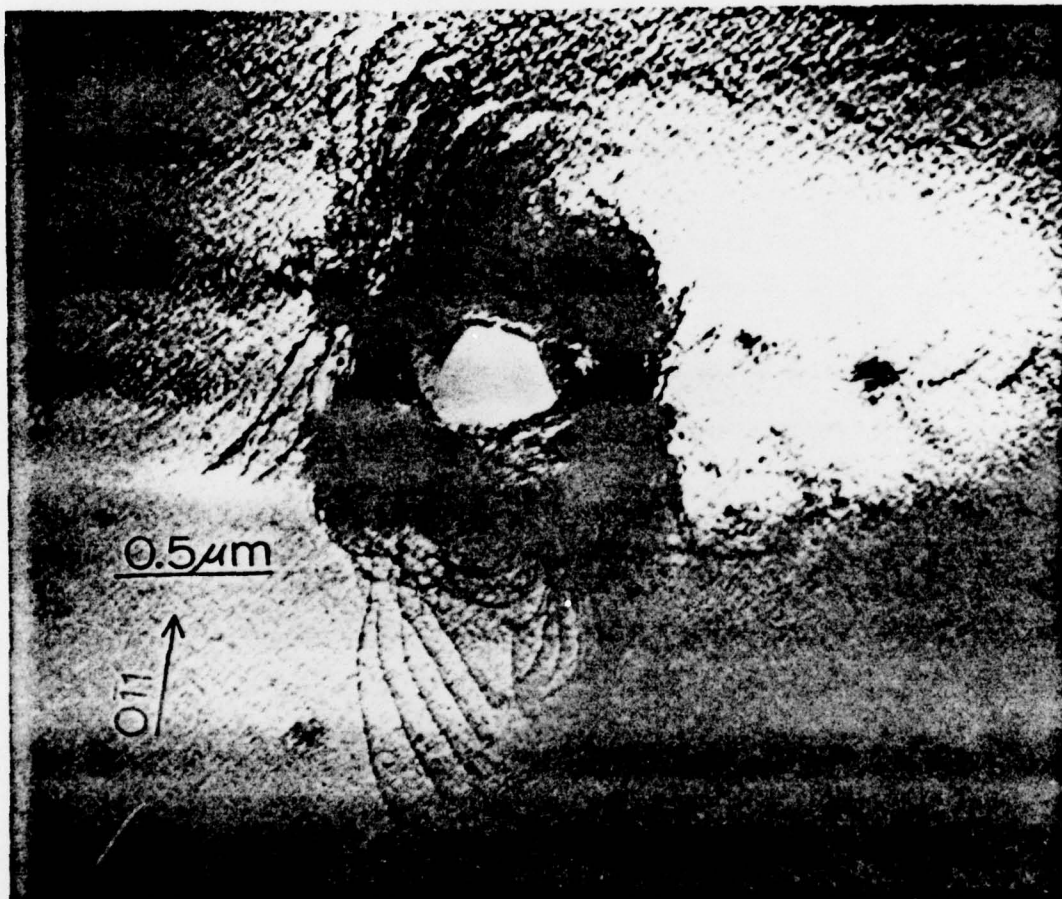
Fig. 4

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Fig. 5



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Fig. 6a

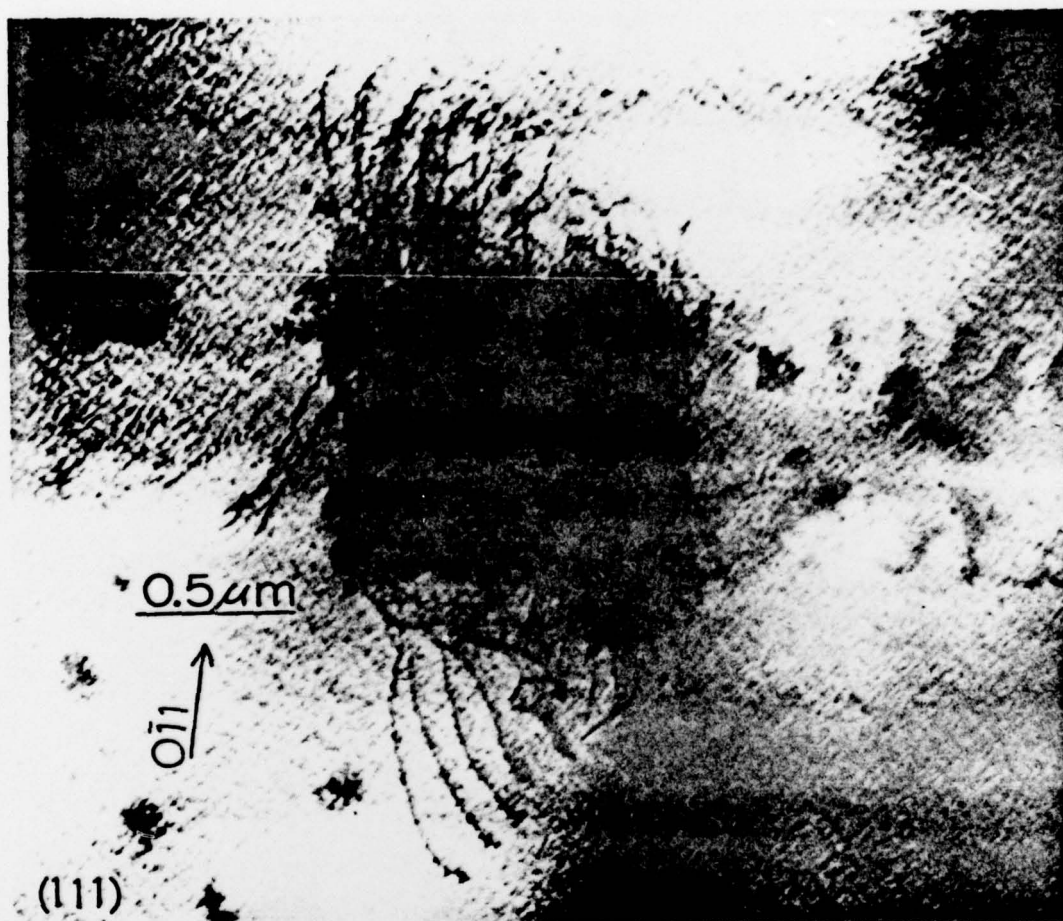


Fig. 6 b

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Fig. 7b

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| 13. ABSTRACT The accommodation effects which accompany hydride precipitation were studied in the Nb-H system using T.E.M. Elastic accommodation and punching of prismatic dislocation loops in the solid solution matrix were observed on precipitation. The reversibility of the plastic accommodation processes was studied. Dislocation generation and motion in the hydride was observed during reversion. These observations were related to the volume changes due to hydride formation and to the thermodynamics of the phase change. Direct evidence for the inhibition of hydride precipitation due to trapping at O and N interstitials is presented. | | |

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